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ON THERMOLUMINESCENCE SPECTRA

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ABSTRACT. The construction of a rapid-scanning spectrophotometer capable of recording spectrum in one second is reported in this paper. The thermoluminescence spectra of KCl and its analysis, along with a brief description of the demountable cathode ray tube and the temperature recording system used in the experiment, are also given.

INTRODUCTION

In studying thermoluminescence it has been found that peaks in the thermoluminescence glow curves differ in the spectral nature of the emission. Up till now all attempts to record spectrographically the spectrum of the thermoluminescence peaks have failed. The failure is due to the transient nature of the glow and its low intensity. In order to make a detailed study of the spectral nature of various thermoluminescence peaks a rapid-scanning of the weak transient emission is necessary. A spectrophotometer suitable for this purpose has been designed and constructed under the guidance of Prof. S. N. Bose. The part of the paper dealing with its design and construction was reported earlier by Prof. Bose at the International Crystallography Conference, held in Paris in July, 1954.

EXPERIMENTAL TECHNIQUE & EQUIPMENT

The apparatus assembly consists of various parts:

(1) For excitation - demountable cathode ray tube fitted with sample holder.

(2) For recording thermoluminescence spectra—a rapid-scanning spectrophotometer with a recording system.

(3) For recording temperature—a thermocouple and a galvanometer.

The construction of the demountable cathode ray tube of pyrex glass will be clear from figure 1. The finely powdered sample is rubbed on the flat surface of the silver bulb of the sample holder without using any adhesive. The upper part of the sample holder is double-walled and made of brass. Close to the surface where the sample is rubbed, a cromel-alumel thermocouple is mounted to give the temperature of the phosphors. Obviously silver is used to minimise any

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temperature difference that may creep in between the phosphor and the thermocouple. Silver specimen-holder, by virtue of its low thermal capacity, is very convenient to heat at a high rate. In the hollow of the silver bulb an electric heater

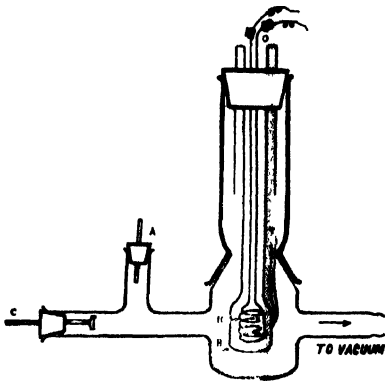

Fig. 1. Diagramatic representation of the demountable cathode-ray tube.
A—Anode,
B—Silver bulb of the sample holder,
C—Cathode,
H—Heater,
T—Thermocouple,
O Opening for pouring liquid oxygen.

is fitted, which is run at 20—30 volts and 20—30 amps. current from a transformer. The double-walled portion of the sample holder passes through a rubber cork (as shown in the figure) which can be fitted in a glass cone. Thus the sample holder can be rotated to expose different faces of it to cathode ray, so that fresh surface can be used when necessary. Liquid oxygen is poured in the bulb of the sample holder through the opening at the top which projects outside the discharge tube. A quartz window is provided in the discharge tube. When a vacuum sufficient for cathode discharge is obtained, the bulb of the sample-holder is filled with liquid oxygen to maintain the sample at the low temperature required.

The cathode ray tube is run by a rectified high voltage power unit operating at 10 KV with electronic current of approximately 400 mA. The advantage of using this rectified H.V. power unit is that it protects the sample from the hazards of ionic bombardments. During the thermoluminescence experiments, the sample is initially bombarded continuously for at least ten minutes, so that all the trapping centres might be saturated.

It is seen that, if the initial bombardment is poor, only the shallow traps are filled, while the deeper traps remain inoperative. Thus the yield of the thermoluminescence glow depends somewhat on the initial bombardment, and hence

irradiation is continued for an appreciable amount of time so that the traps may be filled to saturation.

The spectrophotometer consists of two slits, a 60° quartz prism, two concave mirrors, and a plane mirror of stainless steel. The plane mirror is placed on a turning table which is connected to a cam rotated by a synchronous motor so that the mirror oscillates through 3° (approximately) in 9/10ths of a sec., and flies back again to the initial position instantaneously.

The light emitted by the phosphors is collected by a condensing lens system (one convex and one cylindrical) and is concentrated on the entrance slit of the spectrophotometer and it passes on to the collimating concave mirror. The rays of light rendered parallel by reflection from the collecting concave mirror are dispersed by the quartz prism. The dispersed rays are then received by the plane mirror which reflects the ray to a second concave mirror. The rays after reflection from the concave mirror are focussed on the exit slit. The oscillation of the plane mirror causes the spectrum to sweep in front of the exit slit in 9/10ths of a second and to fly back to the initial position instantaneously. A photomultiplier tube of 19 dynodes and of very high gain transforms the weak spectrum on the exit slit into electrical signals which, after suitable amplification, are displayed on a cathode ray oscillograph. The cam drive also supplies the trigger for the horizontal sweep of the oscillograph which makes every spectrum to start at the left and to end at the right of the screen. Thus in every second a curve of the spectral distribution of the emission is obtained on the oscillograph screen. It is photographed with a specially constructed camera with a 3.5 Tesser lens and autosequence release synchronised with the oscillograph sweep. The spectrum calibration of the record is done by taking reference lines of various known sources e.g., He or Hg discharge lamps. Thus the instrument performs the dual role of a spectrograph and a microphotometer and can be very conveniently adopted to carry on studies of (1) fluorescence and phosphorescence, (2) thermoluminescence spectra, (3) temperature-dependence of luminescence (both fluorescence and phosphorescence), (4) correlation of colour centres and other known trapping centres with luminescence, (5) development of emission centres in the phosphor during X-ray or cathode ray irradiation and (6) near infra-red absorption and emission spectra etc. Minor variations of the experimental technique may extend the usefulness of the present apparatus to many other fields.

The various part of the spectrophotometer as shown in figure 2, are rigidly mounted on a horizontal, square ($20'' \times 20''$) heavy cast iron base, supported on a tripod stand with three levelling screws.

The accuracy of the spectroscopic results depends on the proper alignment of the light source, condensing lens system and the entrance slit of the scanning spectrophotometer in relation to one another and of all of them with respect to the first concave mirror. For this purpose, the condensing lens system and the source are mounted on a heavy optical bench 60 cms. long.

Slits. The slits are formed of a pair of stainless steel jaws of which one is fixed and the other is movable by a micrometer screw with a drum-head having 100 equal divisions on it. The effective pitch of the screw (expressed as slit width per revolution) is 0.5 mm. The screw arrangement is, however, reverse of the usual—the backward motion of the micrometer screw decreasing the width of the slit. The chance of damage to the sharp edges of the jaws under spring pressure

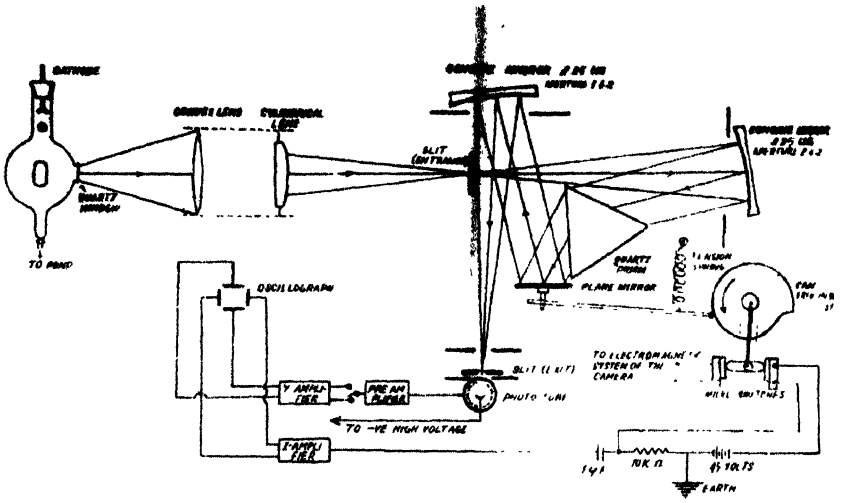

Fig. 2. The apparatus and its experimental set up.

is thus eliminated. The maximum length of the slit is 20 mm., which can be reduced by means of a sliding diaphragm having three apertures for spectrum photography. The slit system is mounted on a stand with facilities of (i) raising and lowering by a rack and pinion arrangement and (ii) tilting around a vertical axis and clamping in position by a fixing nut for proper alignment. To keep the spectrum focussed on the slit, the slit-stand can be moved on a horizontal grooved base provided with a measuring scale. The movement of the stand in this groove is effected by means of a worm screw which enables the slit to be so adjusted that a very sharply focussed spectrum is obtained while the position of the slit is ascertained from the scale. For the purpose of taking photographs of the spectrum on a plate, the exit slit may be replaced by a plate-holder of size.

Concave mirrors. The concave mirrors are of stainless steel having a focal length of 25 cms and aperture $f/4.2$. The collimating concave mirror is placed at a distance of 25 cms from the entrance slit. The mirrors are mounted on a stand with arrangement for raising or lowering them at will (rack and pinion) and also for rotating them about the vertical axis. Additional adjustment facilities are provided for a tight spring and a movable screw which tilts the mirrors

around a horizontal axis. Finally the entire system is fixed to a plate, screwed to the base of the instrument by vertical screws and vertical springs, which make the base of the mirror capable of slight movements around a vertical axis. With these highly flexible arrangements, all possible motions of the mirrors guarantee accurate alignments and correct optical paths, yet obeying the fundamental requirements of rigidity.

Prism and prism table : A 60° quartz prism 4 cms high, is made by cementing together two 30° cornu prisms, one right-handed and the other left-handed The overall refracting base of the prism is 7 cms and the prism is placed on a two-fold circular prism table with three levelling screws. This is mounted on a vertical support provided with a fixing screw to enable the prism table to be fixed at any suitable height and position around the vertical axis. A micrometer screw, with a large drum-head having 100 divisions, makes the prism table amenable to further small adjustments around the vertical axis and is intended to receive and fix any desired spectral range. This movement may be noted from a straight scale held close to the drum head; the desired wavelength region may be extrapolated from the reading of the scale accurately which in turn has been compared and calibrated with different spectral lines.

Plane mirror : The stainless steel plane mirror is clamped on a vertical stand held upright by a cylindrical tube fixed to the base of the instrument. The mirror-stand is rotatable with a jerk-free motion inside the cylindrical tube by means of two sets of ball bearings fitted at different heights. Slightly above the cylindrical tube which holds it, the mirror-stand has a grooved joint where two circular plates are fitted, the bottom one being rivetted to the lower portion of the stand. The upper plate, containing a fiducial mark, may be rotated slightly relative to the lower one containing a graduated scale. This slight motion which is very helpful in the final stages of alignment, is actuated by means of a slide-screw having movements similar (though differing in mechanical details) to those described in connection with the motion of the prism table.

Cam : The plane mirror stand is connected to a shaft (10 cms). The end of the shaft terminates in a small roller having a frictionless drive on ball-bearings. The roller rests on a cam rotating the plane mirror by 3°. To eliminate objectionable mechanical vibrations, the roller and the camedges are lined with rubber.

Camera : The automatic operation of the camera makes it suitable to record the one-second sequence photographs of the spectra displayed on the oscillograph screen. The camera is coupled with a system, electromagnetically operated, which automatically actuates the advance of the film, cocks the shutter to take exposure – all in perfect synchronisation with the oscillograph sweep. The cam drive of the plane mirror operates a micro-switch which in its turn operates the electromagnet system. A magazine of 50 ft. film can be fed into the camera which makes it possible to photograph thermoluminescence spectra of repeated experiments on the same film.

The photomultiplier is enclosed in an aluminium casing with a small window in front of the photo cathode surface. The space between the photomultiplier tube and the casing wall is filled with a dehydrating silicate jelly in order to prevent any surface leakage.

This high gain, low noise photomultiplier of 19 dynodes is run by a highly stabilized power unit giving variable voltages from 200-2800 volts. The outputs of the stabilized units are connected to the bleeder circuit (– ve H.T. terminals to the photocathode) by means of long, shielded cables. There is a meter on the front panel of the stabilized power supply to give directly the voltage applied to to the photomultiplier. As the intensity of the thermoluminescence spectrum is very weak, the photomultiplier out-put current is very very small (only of the the order of 5—10 microamps). This low output current is properly amplified by a high-gain amplifying system. The output of the amplifying system is then applied to the vertical plates of the oscillograph. The amplifying system has three fixed gains which are actuated by a band-switch. All the circuit elements are properly shielded.

For recording temperature during thermoluminescence a micro-moll galvanometer, with a time period of 0.3 sec., which is critically damped with suitable resistance, is used. The movements of the galvanometer are recorded on a strip of 35 mm. film of length 40 cms. The galvanometer exciter lamp is operated by a micro-switch coupled with the external sweep of the oscillograph in such a way that when the oscillograph spot comes to the middle position of the oscillograph screen, the microswitch is set on momentarily and a spot of light from the galvanometer excitor lamp focussed by a cylindrical lens (40 cms long), falls on the film strip. At the beginning of each experiment, a spot in the film strip is obtained at liquid air temperature, which serves as the reference spot and the temperature of any subsequent spot can be obtained by measuring the distance of the spot, under consideration, from the reference spot. A few known temperature (starting from liquid oxygen temperature to 300°C) spots are obtained on the film and the distance of each of these spots is measured from the reference spot corresponding to liquid oxygen temperature. Then a graph, drawn with the temperature in °K against the distance of the spot, serves as the calibration curve. The galvanometer is placed on a highly insulated platform which rests on sand to make it free from vibrations. The galvanometer, with the exciter lamp and the film holder, is placed in a wooden chamber under the working table.

The thermoluminescence glow shows variation due to the different rates of heating of the sample, and, in the initial part of the experiment, the rate of temperature rise depends on the amount of liquid oxygen present in the specimen-holder just at the moment when heating is started. So the sample-holder is filled with liquid oxygen up to a fixed height before heating is started.

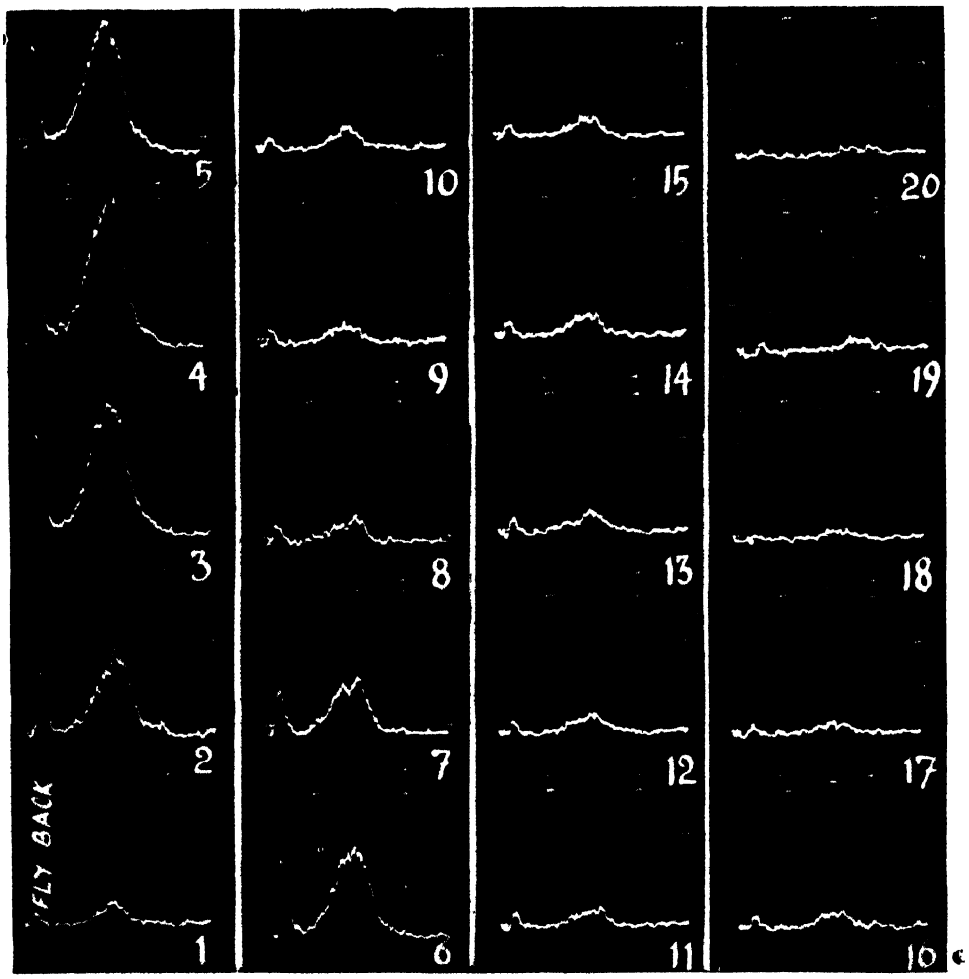

Fig. 3 (a) Thermoluminescence spectra of KCl excited at 90°K.

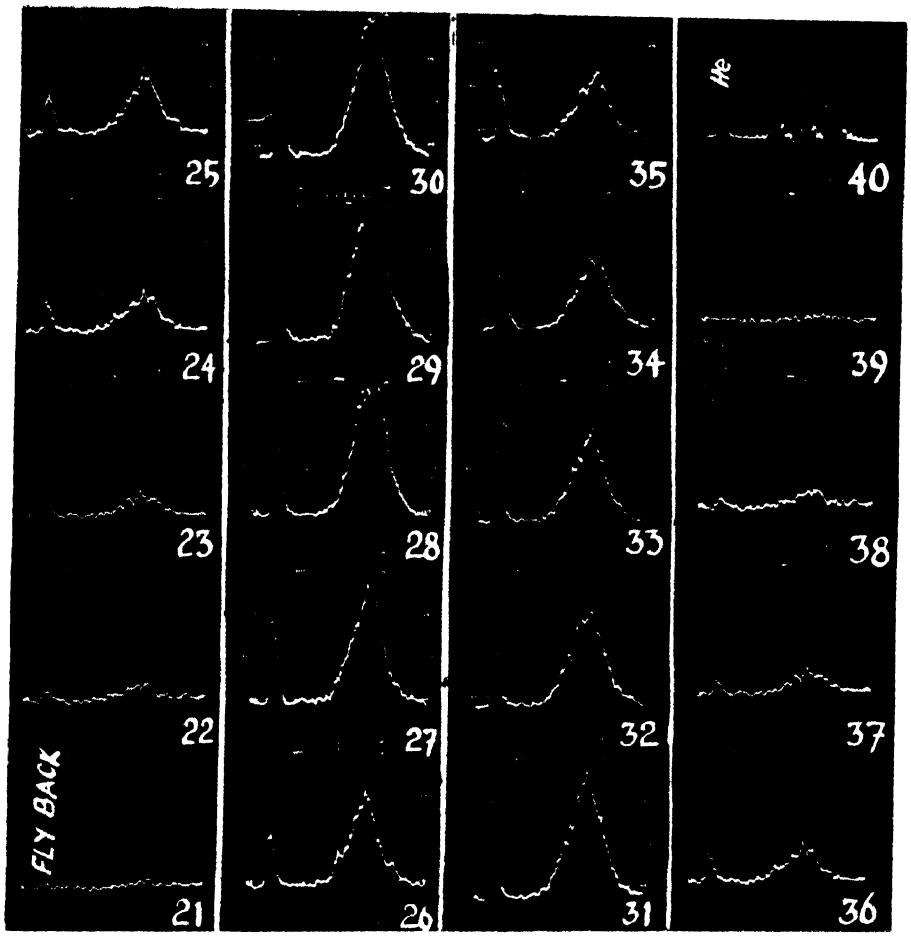

Fig. 3 (b) Thermoluminescence spectra of KCl excited at 90°K.

The experiment is performed in a dark room. After exciting the sample in the dark by cathode rays at liquid oxygen temperature for about 10 minutes or more, the excitation source is cut off. The high voltage power supply for the photomultiplier tube and the heater current of the specimen-holder are switched on. The oscillograph spot-movements are watched, and as soon as the vertical shifts of the oscillograph spot start, the electro-magnet system of the camera and the exciter lamp of the galvanometer are switched on. This is done to save unnecessary wastage of the film. The heating and the recording are continued till the entire stored energy is given out and the sample does not give any more thermoluminescence glow.

EXPERIMENTAL RESULTS

Pure potassium chloride on bombardment with cathode rays at room temperature becomes deep blue and the sample fluoresces weakly. The thermoluminescence glow is too weak for spectroscopic analysis—showing that the energy stored in potassium chloride excited at about 300°K is mostly released by nonradiative mechanism. But this colour at the temperature of liquid oxygen looks pinkish.

The thermoluminescence of potassium chloride excited at 90°K consists of two strong glow peaks at 120°K and 549°K (approximately) and a weaker peak at about 200°K. The peak at 549°K is the strongest. The glow peaks have emissions at different spectral regions. The first thermoluminescence spectrum at 106°K with peak at 434 mμ is recorded in frame No. 1. There is a gradual increase in the height of the peak up to the frame No. 4, wherein it attains maximum intensity having peak at 440 mμ, half-width extension of 383 mμ—483 mμ, at a temperature of 120°K. The shape of the bands in frames No. 3-9 appears to be changing. This may be due to temperatue shifts towards longer wavelengths which is a common phenomenon. In these spectra, weak appearance of longer wavelength band is perceptible which becomes stronger in the high temperature glow peak. It should be mentioned that exact peak positions of the diffused bands are difficult to measure and the measurements become more uncertain where the emission intensity is poor; the measurements are more reliable near the glow peak temperatures. The emission during the second glow peak (at 200°K) is very poor in intensity and the corresponding spectral nature is very diffuse; this may be seen from frame Nos: 12-21. The peak positions and extensions cannot be measured properly; it can, however, be said that the spectral nature of emission during the second glow peak is not the same as those during the first or the third glow peak; emission here consists of short wavelength (blue) part only.

The third glow peak appears at frame No. 22 corresponding to the temperature 479°K, and it attains maximum intensity in frame No. 29; the spectral nature of emission at different stages of this glow peak has been recorded in frames numbering 22-36 i.e., at temperature between 479°K and 619°K. As may be seen

from the figure (frame No. 22-36) and table, there are distinct changes in the peak position of the thermoluminescence emission band during the third glow peak; shifts in the peak positions are not always in the same direction with increase in temperature. At the low temperature end (frame No. 22; temp. 479°K) the emission band shows a peak at 510 mμ; near about the glow temperature (frame No. 28—29; temperature 439°K—549°K) the thermoluminescence is comparatively rich in longer wavelength emission and shows a peak at 525 mμ; at still higher temperature band maximum shifts towards short wavelength, e.g. at 619°K band maximum is at 513 mμ.

TABLE I

Potassium chloride excited at 90°K.

Frame No.	Peak mμ	Half-width mμ	Temperature °K
1	434	—	106
2	432	385—481	110
	590		
3	432	372—483	115
4 (Max)	440	383—483	120
	590		
5	430	380—483	125
6	430	380—483	131
7	409	—	137
	448		
8	409	—	145
	448		
9	430	—	153
10	440	—	161
11	440	—	169
12	440	—	177
13	440	—	185
14—21	(Max. at 200° K corresponding to Frame No. 15)		
22	510	—	479
23	513	—	489
24	513	455—582	499
25	513	453—582	509
26	513	453—582	519
27	513	453 —582	529
28	525 (out of scale)		539
29 (Max)	525 (out of scale)		549
30	525	462—580	559
31	520	462—580	569
32	518	456—602	579
33	515	451—602	589
34	515	451—602	599
35	513	451—602	609
36	513	—	619

Dutton and Maurer (1953) have measured the electrical conductivity of X-rayed potassium chloride during heating of the sample from the low temperatures and have found two conductivity peaks (temp. 128°K and 205°K) associated with changes in colour centres. They have also noticed thermoluminescence accompanying the conductivity peaks.

They have ascribed the peak at 128°K to the destruction of V_1-band. Sharma (1952) has found that the V_0-band disappears with the peak at 205°K; which Dutton and Maurer have ascribed to F'-centre. But in our measurements it is found that the peak at about 200°K is the weakest of the three. Dutton and Maurer have worked with single crystal while Sharma has used powdered sample. Sharma detected the bleaching of the bands by measuring the total diffuse reflectance of light monochromatised by filters. Further, the thermoluminescence curves for potassium chloride recorded by Sharma as also by Bose (1955) are distinctly different from that observed in the present investigation. The second glow peak at 200°K is very poor in intensity compared to the first and third glow peaks, whereas the second glow peak is very strong compared to others in the measurements of Sharma and Bose. This difference in thermoluminescence characteristics may be due to thermal history of the sample and is not well understood at present. The results of the present measurements have better agreement with those of Dutton and Maurer: as such bleaching temperatures reported by these authors are only taken into consideration to interpret the thermoluminescence glow of potassium chloride.

DISCUSSION

Thermoluminescence emission during the first glow peak (120°K) seems to be changing in spectral character with increasing temperature and the short wavelength part (band maximum at 440 mμ) is much more intense compared to longer wavelength band with maximum at 590 mμ (the 590 mμ is only just perceptible in the spectrum). In the next glow peak (at 200°K) the emission is poor and the long wavelength part is no longer perceptible. During the third glow peak (at about 549°K), one of these bands seems to be present in the emission and a strong long wavelength band with maximum at 525 mμ is observed instead. Thus most of the energy is released during this high temperature glow peak. The study of diffuse reflectance measurements show that the highest glow temperature (549° K) of potassium chloride is coincident with the bleaching temperature for F-centres. In this case also we find that bleaching of F-centres is somehow related with thermoluminescence emission, although it is known that optical excitation in F—band does not produce any luminescence. The other two glows peaks occur at the bleaching temperatures of V_1 and F'-centres. The difference in the spectra leads us to the conclusion that the responsible emission mechanisms must be different in each case.

Excitation of potassium chloride at 300°K reduces the luminescence efficiency considerably, so that, on bleaching, intensity of emission is too poor to be recorded. The effect is due to the non-radiative energy levels provided by the higher agreegates of F-centres which are more likely to be produced in this temperature

range. This is a general behaviour with almost all the alkali halides (i.e., intense colouration always reduces the luminescence intensity). In the case of potassium chloride, the effect is very pronounced for excitation at room temperature (300°K).

ACKNOWLEDGMENTS

We are grateful to Prof. S. N. Bose for his valuable guidance and constant interest in the work. Thanks are due to Mr. H. N. Bose for his helpful discussions, and to the Ministry of Education, Government of India, for granting scholarships to both the authors.

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Letter to the Editor

The Board of Editors will not hold itself responsible for opinions expressed in the letters, published in this section. The notes containing reports of new work communicated for this section should not contain many figures and should not exceed 500 words in length. The contributions must reach the Assistant Editor not later than the 15th of the second month preceding that of the issue in which the Letter is to appear. No proof will be sent to the authors.

DIPOLE MOMENTS OF TRI-SUBSTITUTED BENZENES. PART I

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Following the author's previous work on tri-substituted benzenes (Rao, 1955-56) the dipole moments of a few other similar molecules (the substituent groups being Cl and NO_2) are determined in solution in benzene at 30°C. The calculations are extended to include 1, 2, 3 substitution also. The results are presented in the following table.

TABLE

Compound	observed	calculated
2, 4-Dichlorotoluene	1.95 D	1.95
2, 6-Dichlorotoluene	1.11	0.75
3, 4-Dichlorotoluene	2.95	2.82
4-Chloro 2-Nitrotoluene	3.63	3.68
6-Chloro 2-Nitrotoluene	2.95	2.83
4-Chloro 3-Nitrotoluene	4.82	4.88
6-Chloro 3-Nitrotoluene	3.11	2.92
2-Chloro 4-Nitrotoluene	4.05	3.88

It will be seen from the table that the agreement between the calculated and the observed values is satisfactory.

Full details will be communicated shortly.

ACKNOWLEDGMENTS

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